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Sol-Gel-Prepared Nanoparticles of Mixed Praseodymium Cobaltites-Ferrites

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Abstract

Two series of nanocrystalline powders of $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ ($x = 0.1, 0.3, 0.5, 0.7$ and 0.9) of high purity were obtained by sol-gel citrate method at 700 and 800 °C. The formation of continuous solid solution with an orthorhombic perovskite structure (sp. group *Pbnm*) was observed. A peculiarity of the $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ solid solution is the lattice parameter crossovers, which occurred at certain compositions and revealed in the pseudo-tetragonal or pseudo-cubic metric. An average crystallite size of the $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ samples estimated from the analysis of the angular dependence of the X-ray diffraction (XRD) line broadening varies between 30 and 155 nm, depending on the composition and synthesis temperature.

Keywords: Mixed cobaltites-ferrites, Perovskites, Nanopowders, Crystal structure

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Background

Complex oxides with perovskite structure RMO_3 , where *R* and *M* are rare earth and transition metals, respectively, represent an important class of the functional materials. In particular, the “pure” and mixed rare earth cobaltites and ferrites are used in thermoelectric devices; solid oxide fuel cells, as membranes for partial oxidation of methane; and cleaning oxygen, as catalysts and sensory materials [1–5]. The interest in the rare earth cobaltites RCoO_3 is also stimulated by their unique fundamental physical properties, such as different types of magnetic ordering and temperature-induced metal-insulator (MI) transitions conjugated with the spin-state transitions of Co^{3+} ions [6, 7]. These transitions are strongly affected by the chemical pressure caused by the exchange of cations either in *A*- or *B*-sites of perovskite structure [8–10].

Among the mixed rare earth cobaltites-ferrites $\text{RCo}_{1-x}\text{Fe}_x\text{O}_3$, the most extensively studied is a system with La [10–12], whereas information about phase and structural behaviour in the systems with other rare earths is rather limited. Our recent investigations of structural and thermal behaviour of the mixed cobaltites-ferrites with *R*=Pr, Nd, Sm and Eu obtained by a

standard ceramic technique at 1200–1300 °C [13–16] proved a formation of the continuous solid solution with the orthorhombic perovskite structure. In situ high-temperature X-ray synchrotron powder diffraction revealed strong anomalies in the lattice expansion, which are especially pronounced in cobalt-rich specimens. They are reflected in a sigmoidal dependence of the unit cell dimensions, in extra increment of the unit cell volume and in clear maxima of the thermal expansion coefficients [16–19]. These anomalies are related to the changes in spin state of Co^{3+} ions and conjugated MI transitions. They become less pronounced with the decreasing of the cobalt content in the $\text{RCo}_{1-x}\text{Fe}_x\text{O}_3$ series.

Here, we report the results of structural characterization of nanocrystalline cobaltites-ferrites $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ prepared by sol-gel citrate route.

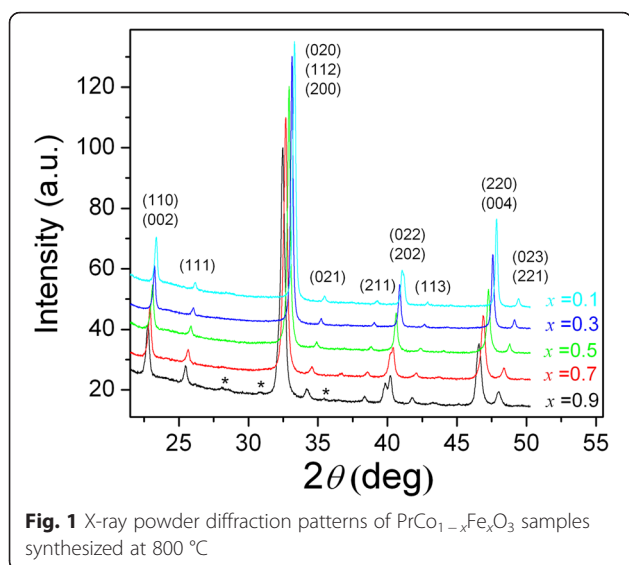
Methods

Nanocrystalline powders of $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ ($x = 0.1, 0.3, 0.5, 0.7$ and 0.9) were prepared by sol-gel citrate method. Crystalline $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.99 %, Alfa Aesar), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (ACS, Alfa Aesar), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (ACS, Alfa Aesar) and a citric acid (CC) were dissolved in water and mixed in the molar ratio of $n(\text{Pr}^{3+}):n(\text{Co}^{2+}):n(\text{Fe}^{3+}):n(\text{CC}) = 1:(1-x):x:4$ according to the $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ nominal compositions. Prepared solutions were gelled at ~90 °C and

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subsequently treated at the temperatures of 700 and 800 °C for 2 h. Thus, two series of the samples were obtained. Spot-check examination of the cationic composition of the samples was performed by energy dispersive X-ray fluorescence (EDXRF) analysis by using XRF Analyzer Expert 3L.

Laboratory X-ray powder diffraction investigation was performed on the Huber imaging plate Guinier camera G670 ($\text{Cu } K_{\alpha 1}$ radiation, $\lambda = 1.54056 \text{ \AA}$). The high-resolution X-ray synchrotron powder diffraction examination was performed for the $\text{PrCo}_{0.5}\text{Fe}_{0.5}\text{O}_3$ @700 °C and $\text{PrCo}_{0.5}\text{Fe}_{0.5}\text{O}_3$ @800 °C samples with equiatomic amount of Co and Fe. Corresponding experiments were carried out at the beamline

ID22 of ESRF (Grenoble, France) during the beam-time allocated to the Experiment N° MA-2320. All crystallographic calculations were performed by means of the programme package WinCSD [20], which was also used for the evaluation of microstructural parameters of the samples. The average grain size of the powders (D) and lattice strains $\langle \epsilon \rangle = \langle \Delta d \rangle / d$ were estimated from the analysis of angular dependence of the X-ray diffraction (XRD) profile broadening by using the external Si standard for the correction of instrumental broadening. The morphology of the nanoaggregates was investigated by scanning electron microscopy (SEM) by means of an ESEM FEI Quanta 200 FEGi system operated in a low-vacuum mode (70 Pa) and at an acceleration voltage of 15 kV (FEI Company, Eindhoven, NL). The samples were mounted onto conductive carbon tapes adhered on aluminium holders. High-resolution images were obtained using an Everhart-Thornley detector (ETD) for secondary electrons or a solid-state backscattered electron (SSD-BSE) detector.

Results and Discussion

According to X-ray powder diffraction examination of both series of the mixed cobaltites-ferrites $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ obtained at 700 and 800 °C, all the samples synthesized were single phase and possess an orthorhombic perovskite structure isotypic with GdFeO_3 (Fig. 1). Only in the iron-rich specimen $\text{PrCo}_{0.1}\text{Fe}_{0.9}\text{O}_3$ @800 °C the traces of the unidentified parasitic phases could be detected. EDXRF examination of the sample with nominal composition $\text{PrCo}_{0.5}\text{Fe}_{0.5}\text{O}_3$ revealed 70.96(9) wt.% of Pr, 14.98(7) wt.% of Co and 14.06(7) wt.% of Fe, which corresponds to 0.998(2):0.503(3):0.499(3) molar ratio of the metal components.

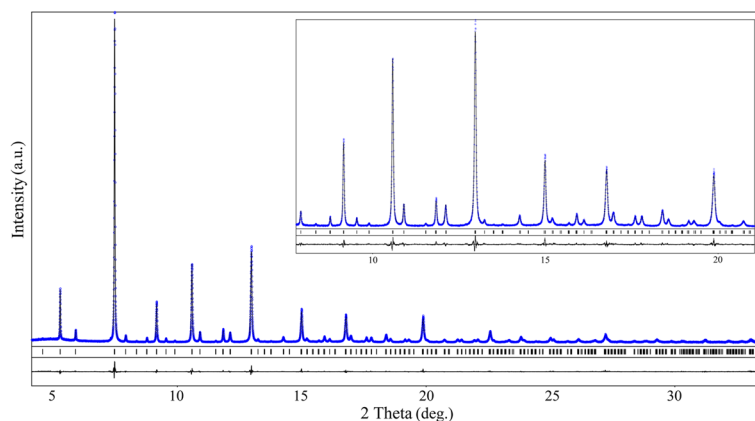


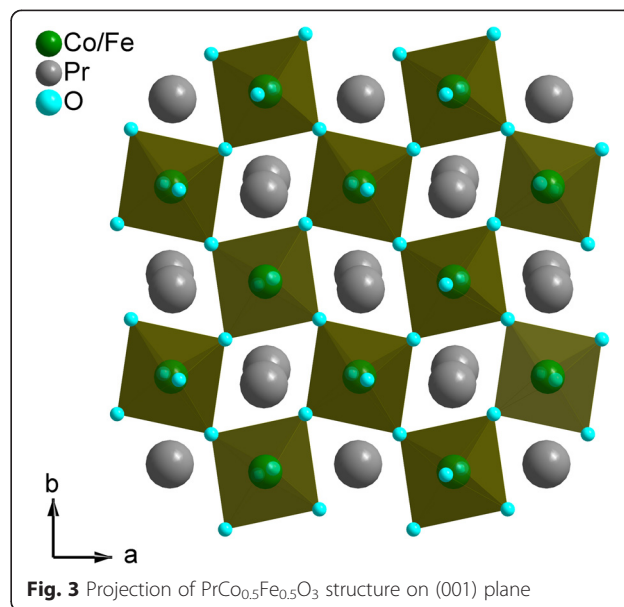
Table 1 Lattice parameters, coordinates and displacement parameters of atoms in $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ (space group *Pbnm*)

Atoms, sites	Parameters, residuals	<i>x</i> in $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$					
		0.1	0.3	0.5 (Lab-XRD)	0.5 (Synch-XRD)	0.7	0.9
Pr, 4c	<i>a</i> , Å	5.3845(2)	5.4044(2)	5.4281(2)	5.4290(1)	5.4544(2)	5.4767(2)
	<i>b</i> , Å	5.3559(2)	5.3944(1)	5.4406(2)	5.4413(1)	5.4980(2)	5.5519(2)
	<i>c</i> , Å	7.5903(3)	7.6297(2)	7.6735(3)	7.6759(2)	7.7246(3)	7.7699(3)
	<i>x</i>	−0.0035(4)	−0.0042(4)	−0.0026(7)	−0.0059(2)	−0.0057(4)	−0.0066(3)
	<i>y</i>	0.02944(9)	0.03134(9)	0.0334(1)	0.03285(8)	0.0380(1)	0.0427(1)
	<i>z</i>	¼	¼	¼	¼	¼	¼
Fe/Co, 4b	<i>B</i> _{iso} , Å ²	0.78(1)	1.02(1)	1.02(2)	0.699(6)	1.18(2)	1.19(2)
	<i>x</i>	0	0	0	0	0	0
	<i>y</i>	½	½	½	½	½	½
	<i>z</i>	0	0	0	0	0	0
	<i>B</i> _{iso} , Å ²	0.94(2)	1.03(2)	0.64(3)	0.43(2)	0.71(3)	0.61(3)
	<i>x</i>	0.053(2)	0.036(2)	0.031(3)	0.063(2)	0.044(2)	0.091(2)
O1, 4c	<i>y</i>	0.4966(10)	0.4960(8)	0.4992(11)	0.4866(10)	0.4926(10)	0.4856(12)
	<i>z</i>	¼	¼	¼	¼	¼	¼
	<i>B</i> _{iso} , Å ²	0.37(8)	0.656(3)	0.885(4)	1.8(3)	0.857(2)	0.977(3)
	<i>x</i>	−0.2937(12)	−0.3070(12)	−0.302(2)	−0.2866(11)	−0.3017(14)	−0.2767(15)
	<i>y</i>	0.2772(14)	0.2771(14)	0.277(2)	0.2787(11)	0.2861(14)	0.3013(12)
	<i>z</i>	0.0382(10)	0.0440(10)	0.0496(13)	0.0426(8)	0.4482(10)	0.4651(11)
O2, 8d	<i>B</i> _{iso} , Å ²	0.37(8)	0.656(2)	0.885(3)	0.75(12)	0.857(2)	0.977(2)
	<i>R</i> _f	0.042	0.047	0.054	0.039	0.061	0.043
	<i>R</i> _p	0.088	0.092	0.123	0.091	0.112	0.125

Full profile Rietveld refinement, performed in space group *Pbnm*, led to an excellent agreement between calculated and experimental profiles for all $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ samples. In the refinement procedure, the unit cell dimensions and positional and displacement parameters of atoms were refined together with background and peak profile parameters and correction of absorption and instrumental zero shift. No significant difference in the structural parameters was found between two series of the samples.

Precise high-resolution X-ray synchrotron powder diffraction examination confirms phase purity of $\text{PrCo}_{0.5}\text{Fe}_{0.5}\text{O}_3$ samples obtained at 700 and 800 °C. No traces of foreign phases were detected in both samples even applying this very sensitive diffraction technique.

In spite of superb resolution (typical HWFM of the reflections of Si standard are in the limits of 0.003–0.006 2 θ°), no reflection splitting was observed at the $\text{PrCo}_{0.5}\text{Fe}_{0.5}\text{O}_3@700^\circ\text{C}$ and $\text{PrCo}_{0.5}\text{Fe}_{0.5}\text{O}_3@800^\circ\text{C}$ diffraction patterns due to the rather pseudo-cubic metric of the orthorhombic lattice and essential nanocrystalline size effect on the XRD line broadening.



However, structural parameters of both samples were successfully refined by the full profile Rietveld method in space group *Pbnm*. As an example, the graphical results of the Rietveld refinement of $\text{PrCo}_{0.5}\text{Fe}_{0.5}\text{O}_3$ @800 °C structure are presented in Fig. 2.

Table 1 contains the results of the Rietveld refinement of the $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ samples obtained at 800 °C by using laboratory X-ray and synchrotron powder diffraction data.

Similar to the “pure” PrCoO_3 and PrFeO_3 compounds, crystal structure of the mixed cobaltites-ferrites $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ can be described as a framework of corner-shared MO_6 ($M = \text{Co/Fe}$) octahedra with the Pr atoms occupying holes between them. A projection of the $\text{PrCo}_{0.5}\text{Fe}_{0.5}\text{O}_3$ structure along [001]-direction is shown in Fig. 3.

The analysis of the concentration dependence of the unit cell dimensions of the sol-gel-obtained $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ samples (Fig. 4, solid symbols) proves the formation of continuous solid solution, similar to those observed recently for the mixed praseodymium cobaltites-ferrites obtained by standard ceramic technique (Fig. 4, open symbols) [13, 16]. Peculiarity of the $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ solid solution is a lattice parameter crossover that occurred at a certain composition, which becomes apparent in the pseudo-tetragonal or pseudo-cubic unit cell dimensions (Fig. 4). The reason for this phenomenon, which was earlier also observed in the related rare earth aluminates, gallates and titanates-

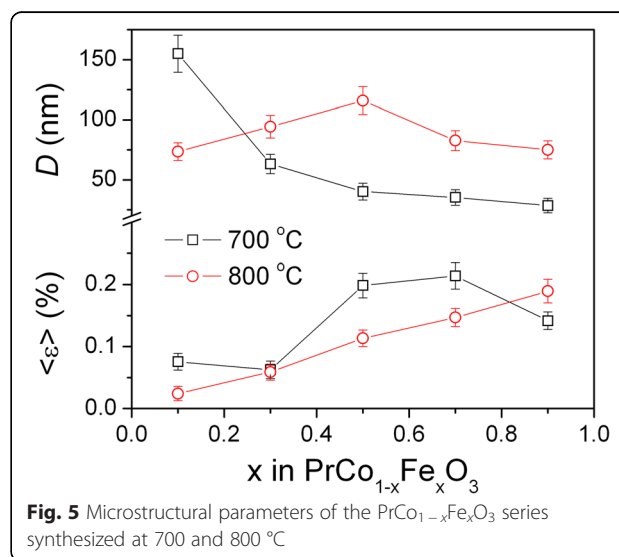
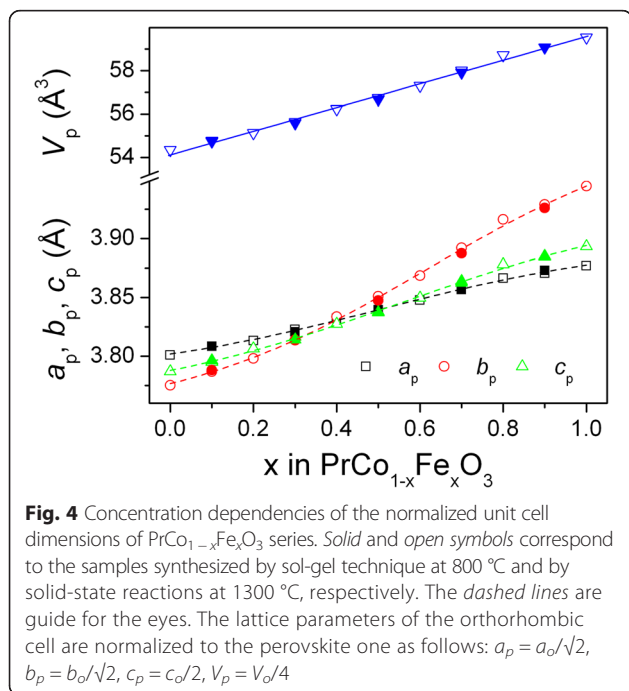
chromites [21–26], is the different cell parameter ratios within the same orthorhombic GdFeO_3 type of structure observed for the end members of these series.

Microstructural parameters of two $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ series synthesized at 700 and 800 °C were evaluated from the analysis of the XRD profile broadening by using the external Si standard. Average grain size D in both series is estimated to vary within the limit of 30–155 nm, depending on the composition and synthesis temperature (Fig. 5). The D values in the $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ @700°C samples systematically decrease with the increasing of iron content, whereas in the $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ @800°C series, this parameter goes through the maximum at $x = 0.5$. In both series, the increase of the lattice strains is observed with increasing iron content (Fig. 5).

Scanning electron microscopy investigation of the $\text{PrCo}_{0.5}\text{Fe}_{0.5}\text{O}_3$ sample prepared at 800 °C (Fig. 6) revealed a lacy morphology of the powder consisting of irregular shaped 60–100-nm nanoparticles.

Conclusions

Two series of the nanocrystalline mixed cobaltites-ferrites $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ ($x = 0.1, 0.3, 0.5, 0.7$ and 0.9) of high phase purity were prepared by sol-gel citrate method at 700 and 800 °C. The average grain size of the powders estimated from the analysis of angular dependence of the XRD line broadening varies between 30 and 155 nm, depending on the composition and synthesis temperature. Refined structural parameters of the $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ @700 °C and $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ @800 °C series prove the formation of continuous solid solution as it was shown earlier for the similar series obtained by the standard ceramic technique at 1300 °C. In comparison



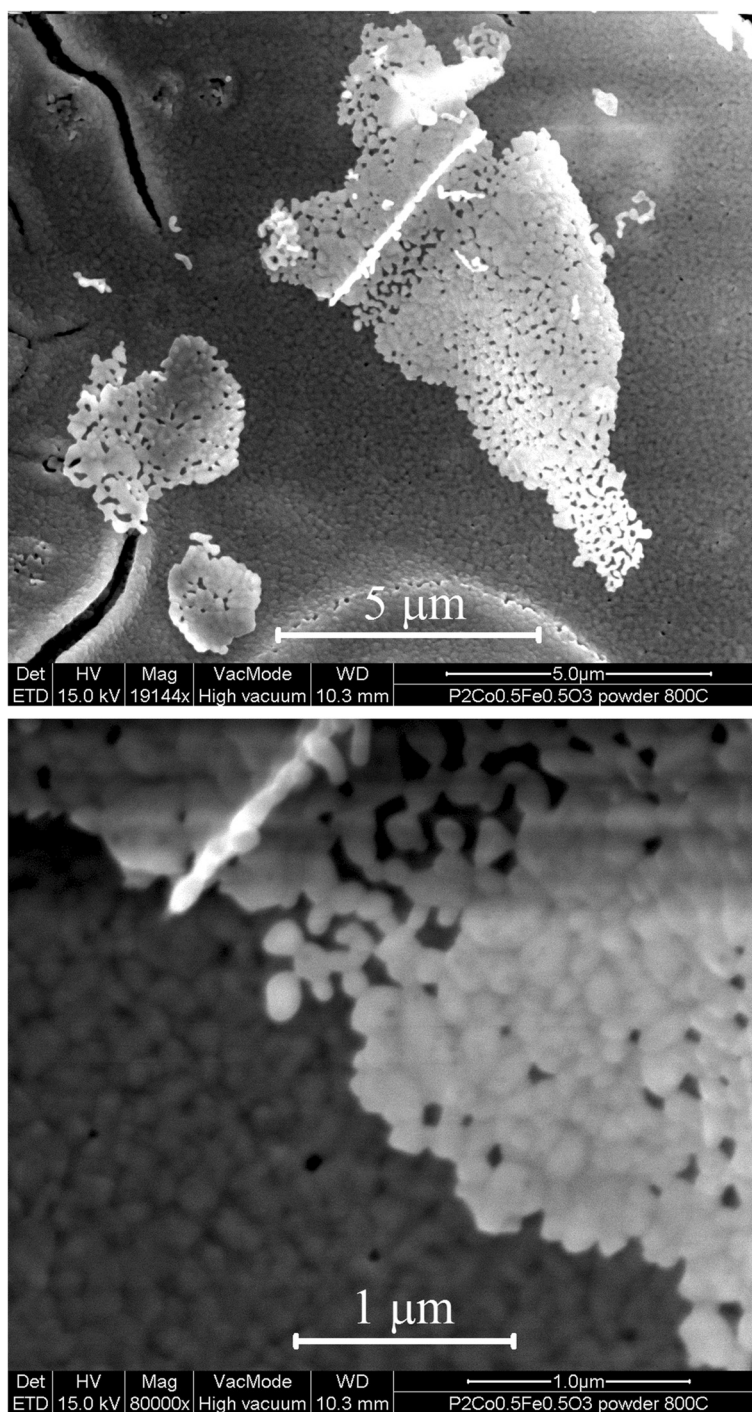


Fig. 6 Scanning electron microscopy of $\text{PrCo}_{0.5}\text{Fe}_{0.5}\text{O}_3$ @ 800 °C. Both images were done with secondary electrons

with a traditional energy- and time-consuming high-temperature solid-state synthesis technique, the low-temperature sol-gel citrate method is a very promising tool for the obtaining of fine powders of the mixed perovskite oxide materials, free of contamination of constituent metal oxides or other parasitic phases.

Competing Interests

The authors declare that they have no competing interests.

Authors' Contributions

OP evaluated the XRD data and wrote the manuscript. LV performed structural characterization of the samples and contributed to the manuscript writing. IL and YV performed the sol-gel synthesis of the

samples. YP contributed to the X-ray and synchrotron diffraction measurements. WCC performed the scanning electron microscopy measurements. All authors read and approved the final manuscript.

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